

Accelerating the Graphitization Process of Polyimide by Addition of Graphene

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ABSTRACT: In this article, a composite film from polyimide and thermally exfoliated graphene was prepared through *in situ* polymerization, and the weight percent of thermally exfoliated graphene with respect to the polyimide monomers was 5 wt %. The film was carbonized at 1000°C for 1 h and then heat-treated at various temperatures up to 2100°C. For comparison, the corresponding pure polyimide film was also prepared and heat-treated at the same condition. It was found that the addition of graphene could effectively prevent the polyimide film from shrinking in the direction parallel to the film surface during the heat treatment. Furthermore, the results of density, X-ray diffraction, shrinkage in the direction perpendicular to the film surface and scanning electron microscopy revealed that the graphitization process of the polyimide could be accelerated by addition of graphene obviously. In view of the above phenomena, a reasonable explanation was presented. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, 132, 41274.

KEYWORDS: carbonization; internal stress-assisted graphitization; polyimide/graphene composite; shrinkage

INTRODUCTION

As an important industrial product, graphite film has been used as thermal diffusion material, heat resistant sealing material, gasket, electromagnetic interference shielding material, and separator for fuel cell because of its excellent resistance to heat and chemicals, high thermal diffusion property, high electrical conductivity, low thermal expansion coefficient, and low permeability of gasses.^{1–5} For example, electronic devices, as represented by a personal computer and a portable telephone, have been requested to have higher performance and smaller size in recent years. With this request, the performance and density of electronic components are increased. But conversely, the amount of generated heat tends to be larger and the space where a fan should be inserted is limited. Thus, graphite film with high thermal diffusion property has been regarded as a satisfying choice and used in a variety of electronic devices.⁵

For the present, commercially available graphite film could be manufactured by an expansion method in which expanded graphite is compressed and a pyrolysis method in which carbonization of carbon precursors (such as polyimide, polyoxadiazole, polyphenylenevinylene, polybenzoxazole, and polyamide) and then graphitization are performed.^{6,7} Compared with graphite film obtained by the expansion method, graphite film obtained by the pyrolysis method has higher thermal diffusivity, mechanical strength, and flexibility. Furthermore, it is easy to

produce a thin graphite film having a thickness of 50 μm or less through the pyrolysis method, which is difficult to achieve through the expansion method.^{6,7} However, the graphitization process in the pyrolysis method always requires long-time heat treatment at extremely high temperature.⁴

Many researchers have already noted that the graphitization process of carbon could be accelerated in the presence of some additives.^{8–14} Noda et al. studied the graphitization process of coke with calcium hydroxide as a catalyst, and they found the graphitization of coke started at a temperature as low as 800°C with the coexistence of calcium hydroxide.⁸ This result was amazing because the coke graphitizes only above 2500°C without additive under atmospheric pressure. Matsuo and Fuertes indicated that Ni was a very effective catalyst to convert carbon into graphite at low temperature.^{13,14} However, the residual additives are usually harmful for the further application of graphite.¹²

The graphitization process of carbon could also be accelerated under external pressure or internal stress.^{15,16} The graphitization of carbons under external pressure was first shown using a carbon derived from coke at a temperature of 1600°C under a pressure of 1 GPa.¹⁷ Subsequent study showed that the pressure could be reduced to 0.3 GPa.¹⁸ Furthermore, even carbons which are nongraphitizable under atmospheric pressure, such as a carbon derived from phenolic resin, can also be converted to graphite at around 1600°C under pressure.¹⁹ Experimentally, it

has been proven that the internal stress can develop in composites of reinforcements and carbon precursors during the carbonization process of carbon precursors and then accelerate the graphitization process of carbon precursors.^{16,20–22} However, because the internal stress accumulated in the carbon precursors decreases as the distance from the reinforcement increases, the acceleration of graphitization tends to occur at the interface between reinforcements and carbon precursors.^{16,20,22}

Graphene is a single layer of graphite and is one of the stiffest (modulus ~ 1 TPa) and strongest (strength ~ 100 GPa) materials.^{23,24} It is reasonable to assume that, accumulation of internal stress could also occur in composites of graphene and carbon precursors during the carbonization process of carbon precursors, which ultimately accelerates the graphitization process of the carbon precursors. What is more, graphene has a high specific surface area,²⁵ which could generate sufficient stress centers to achieve a high graphitization degree of carbon precursors at low temperature. It is well-known that Kapton (registered tradename, EI du Pont de Nemours & Co.) synthesized from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) is a commercially available polyimide film and is widely used as a carbon precursor for the preparation of graphite film. It has simple carbonization and graphitization behaviors but requires very high temperature (usual in a temperature range of 2800°C or higher) to transform into high quality graphite film.^{26–28} For reasons noted above, in the present study, a composite was prepared, in which graphene was chosen as the reinforcement and aromatic polyimide PMDA/ODA was chosen as the carbon precursor. The graphitization behavior of the polyimide in the composite was systematically investigated to clarify the effect of graphene on it.

EXPERIMENTAL

Materials

PMDA and ODA were purified by sublimation in vacuum. *N,N'*-dimethylacetamide (DMAc) was distilled under vacuum over calcium hydride (CaH_2) and stored over 4 Å molecular sieves. Thermally exfoliated graphene with a specific surface area of 758 m^2/g , an average thickness of 0.9 nm, and a C/O atomic ratio of 5.0 was prepared according to the method described in our previous work.²⁹

Measurements

Fourier transform infrared (FTIR) spectra were recorded with a Thermo Nicolet 6700 FTIR spectrometer. The dispersion and distribution of thermally exfoliated graphene in the polyimide matrix were studied with a Tecnai F20 transmission electron microscopy (TEM) at an accelerating voltage of 100 kV. Before the TEM observation, the polyimide/graphene composite film was embedded in the epoxy resin and then cut into ultrathin slices with thickness of 70 nm. The apparent densities of polyimide and polyimide/graphene composite films heat-treated at different temperatures were calculated from film thickness, area, and weight. The X-ray diffraction (XRD) measurement of the polyimide and polyimide/graphene composite films heat-treated at different temperatures was undertaken on a Bruker D8 Advance with Cu K α radiation (40 kV, 40 mA) at a scanning rate of 5°/min from 5 to 50°. The cross-section morphologies of the polyimide and polyimide/graphene composite films heat-

treated at different temperatures were observed with Hitachi S-4800 scanning electron microscope (SEM).

Preparation of Polyimide Film

ODA (2.0024 g, 10.0 mmol), PMDA (2.1812 g, 10.0 mmol), and dried DMAc (60 mL) were added into a flask and the mixture was stirred at room temperature under nitrogen atmosphere. After 24 h, the resulting viscous poly(amic acid) solution was cast onto a glass plate. The glass plate was placed in an oven at 55°C for 2 h to slowly remove most of the solvent under flowing air and then subjected to scheduled heating at 100, 200, 300, and 350°C for 1 h at each temperature under flowing nitrogen. After slow cooling to room temperature, the resulting film was released from the glass surface by being soaked in water.

Preparation of Polyimide/Graphene Composite Film

Thermally exfoliated graphene (0.2092 g) was dispersed in dried DMAc (210 mL) by ultrasonication for 3 h. Then, ODA (2.0024 g, 10.0 mmol) and PMDA (2.1812 g, 10.0 mmol) were added and the mixture was stirred at room temperature under nitrogen atmosphere. After 24 h, about 150 mL DMAc was removed by vacuum distillation and the resulting viscous poly(amic acid) solution was cast onto a glass plate. The glass plate was subjected to the same heat treatment as that given to the polyimide film described earlier.

Heat Treatment of Polyimide and Polyimide/Graphene Composite Films

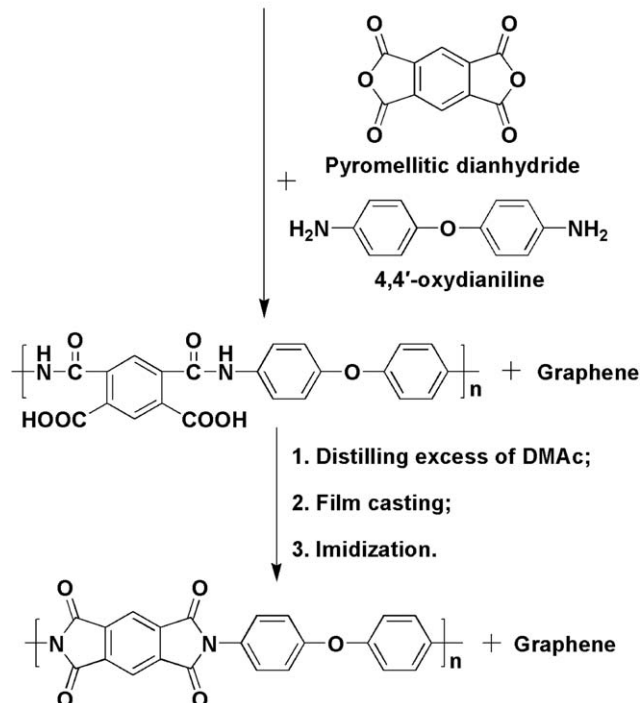
The prepared polyimide film and polyimide/graphene composite film were cut into a square shape and sandwiched between polished artificial graphite plates. Then, they were heated to 1000°C at a heating rate of 5°C/min and carbonized at the temperature for 1 h in a flow of nitrogen. After cooling to room temperature, the carbonized films were sandwiched again between polished artificial graphite plates and heated at 1500, 1800, and 2100°C for 1 h in a flow of nitrogen.

RESULTS AND DISCUSSION

Preparation of Polyimide and Polyimide/Graphene Composite Films

The polyimide film was prepared in accordance with the conventional two-step method by the polycondensation reaction of dianhydride PMDA and diamine ODA to form poly(amic acid) followed by thermal imidization. The preparation of polyimide/graphene composite film was to achieve controlled graphene dispersion and distribution in the polyimide matrix. Typically, three approaches are commonly adopted to prepare polymer/graphene composites: solution mixing, melt blending, and *in situ* polymerization.³⁰ Considering that the polyimide PMDA/ODA is infusible and insoluble because of its rigid chain structure and strong interchain interaction, the *in situ* polymerization was used for the preparation of polyimide/graphene composite film. Scheme 1 demonstrates the steps. The weight percent of the thermally exfoliated graphene was 5 wt % with respect to the dianhydride and diamine monomers. Suspension of the thermally exfoliated graphene in DMAc (1.0 mg/mL) was first prepared by ultrasonication treatment, and then mixed with PMDA and ODA. After being stirred for 24 h, excess of solvent was distilled off to obtain viscous poly(amic acid)/

Dispersing graphene sheets in DMAc solvent



Scheme 1. *In situ* polymerization pathway of polyimide/graphene composite film.

graphene solution, which was then cast on glass and imidized. The complete imidization of poly(amic acid) was confirmed by FTIR spectroscopy. The resulting polyimide film and polyimide/graphene composite film had a thickness of around 30 μm. The dispersion and distribution of the thermally exfoliated graphene in polyimide matrix was investigated by TEM. As indicated by the TEM micrograph in Figure 1, graphene sheets were homogeneously dispersed in polyimide matrix and there were almost no large aggregates. Furthermore, obvious orientation of gra-

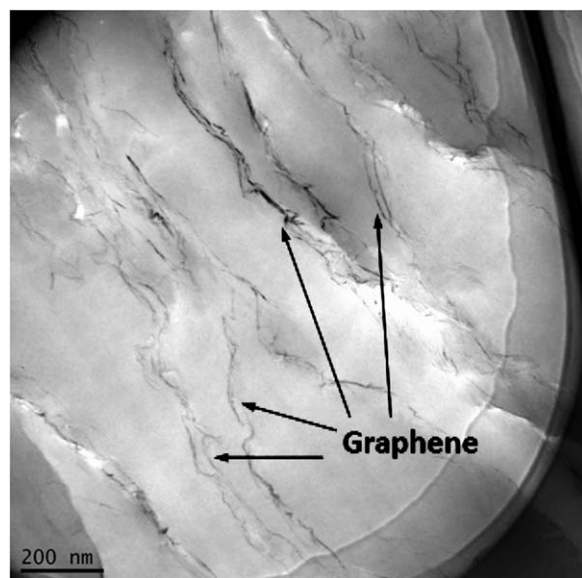


Figure 1. TEM micrograph of polyimide/graphene composite film.

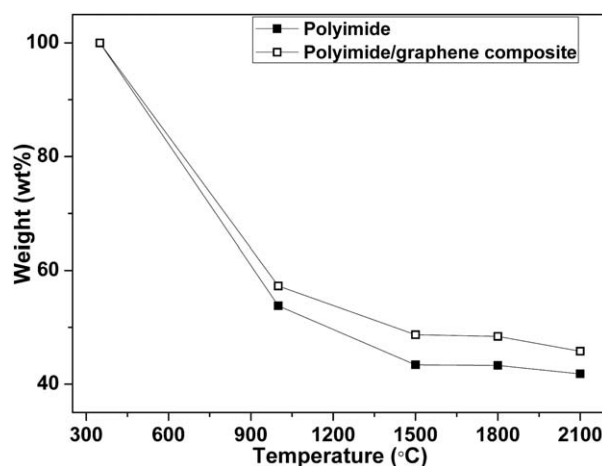


Figure 2. The changes in weights of polyimide and polyimide/graphene composite films with heat treatment temperature in a flow of nitrogen.

phene sheets along the film surface was observed. This could be attributed to the high thermal expansion coefficient of glass, which induced the orientation of polyimide molecular chains and also graphene sheets during imidization.²⁶

Physical Changes During Heat Treatment of Polyimide and Polyimide/Graphene Composite Films

The prepared polyimide and polyimide/graphene composite films were carbonized at 1000°C for 1 h, and then these films were further subjected to heat treatment at 1500, 1800, and 2100°C for 1 h in a flow of nitrogen. After heat treatment at different temperatures, films without any appreciable cracks were obtained. The color of heat-treated polyimide films was shiny black, while the heat-treated polyimide/graphene composite films showed silvery luster.

Many researchers have so far studied the pyrolysis behavior of polyimide PMDA/ODA, and some decomposition mechanisms have been already proposed.^{31–34} During pyrolysis, several thermally controlled chemical reactions take place, such as bond cleavage, release of gaseous byproducts (CO, CO₂, H₂, N₂, and CH₄), intermolecular coupling, and intramolecular coupling. As a result of these various chemical reactions, the polyimide exhibits weight loss and dimension change during heat treatment. The changes in weights of polyimide and polyimide/graphene composite films with heat treatment temperature are shown in Figure 2. The weight loss pattern of the polyimide/graphene composite film followed the weight loss pattern exhibited by pure polyimide film. As prepared graphene had higher char yield than polyimide, polyimide/graphene composite film showed higher residual weight than polyimide film when was heated at the same temperature.

Figure 3 shows plots of shrinkages in the direction parallel to the film surface versus heat treatment temperature for the polyimide and polyimide/graphene composite films. After heat treatment at 1000°C for 1 h, the polyimide film showed shrinkage in the direction parallel to the film surface of 21.8%, which was almost the same as the data of commercial Kapton film reported by others.³¹ In fact, for polyimide PMDA/ODA, its shrinkage in the direction parallel to the film surface mainly occurred over a

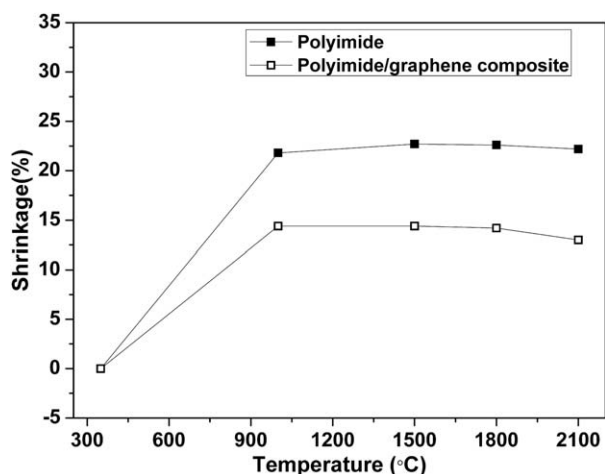


Figure 3. Shrinkages in the direction parallel to the film surface versus heat treatment temperature for polyimide and polyimide/graphene composite films.

rather narrow temperature range of 550–650°C.³¹ So, when the temperature was further increased to above 1000°C, the shrinkage change in the direction parallel to the film surface was small. For polyimide/graphene composite film, the shrinkage in the direction parallel to the film surface was about 14% after heat treatment at 1000°C for 1 h and remained nearly constant when further heated to higher temperature, showing much lower shrinkage than the polyimide film. From the TEM micrograph of polyimide/graphene composite film in Figure 1, there was a preferred orientation of tough and rigid graphene parallel to the film surface, which should be responsible for the lower shrinkage of polyimide/graphene composite film.

Figure 4 shows plots of shrinkages in the direction perpendicular to the film surface versus heat treatment temperature for the polyimide and polyimide/graphene composite films. For both samples, their shrinkages in the direction perpendicular to the film surface increased as the heat treatment temperature increased. This trend was also reported by Bourgerette et al.³⁵ Compared with the polyimide film, the polyimide/graphene

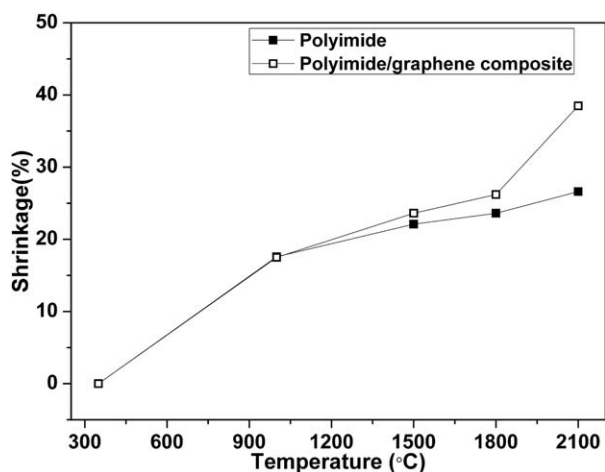


Figure 4. Shrinkages in the direction perpendicular to the film surface versus heat treatment temperature for polyimide and polyimide/graphene composite films.

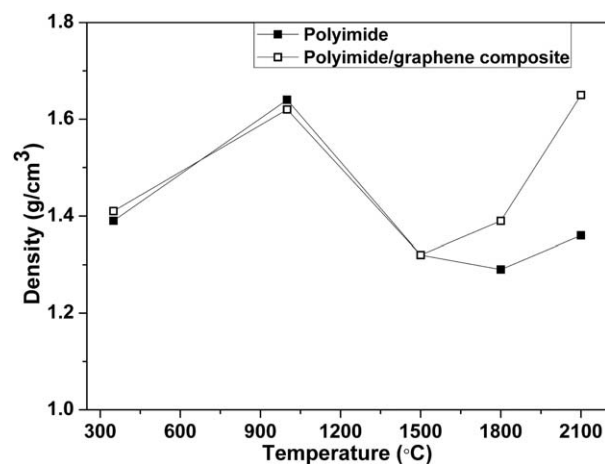


Figure 5. Density versus heat treatment temperature for polyimide and polyimide/graphene composite films.

composite film showed much higher shrinkage in the direction perpendicular to the film surface after heat treatment at 2100°C for 1 h. As graphitization is a process of improving the stacking regularity that is accompanied by volume decrease and a tremendous decrease in thickness of commercial Kapton film was observed during its graphitization process,^{15,16,35} the above phenomenon indicated that the polyimide in the polyimide/graphene composite film may experience some degree of graphitization at 2100°C with the assistance of graphene.

Figure 5 shows plots of densities versus heat treatment temperature for the polyimide and polyimide/graphene composite films. The measured density of polyimide film was 1.39 g/cm³. It was in good agreement with the value of commercial Kapton film (1.42 g/cm³).³⁶ The polyimide/graphene composite film also had similar density (1.41 g/cm³) to the pure polyimide film. For both samples, their density increased from around 1.40 g/cm³ to around 1.60 g/cm³ after heat treatment at 1000°C for 1 h. In the range 1000–1500°C, their densities decreased significantly (from around 1.60 to 1.32 g/cm³). The downward trend in density with increasing heat treatment temperature was also reported by Kipling and Zaldivar, and they attributed this to the result of formation of micropore.^{21,37} After being heat-treated at 2100°C for 1 h, the density of polyimide/graphene composite film increased to 1.65 g/cm³, which was much higher than the corresponding value of polyimide film (1.36 g/cm³). Graphitization is a process of transforming disordered carbon structure into perfectly stacked graphite, which is highly crystalline and has a theoretical density of 2.26 g/cm³.³⁸ The higher density of 2100°C-treated polyimide/graphene composite film than 2100°C-treated polyimide film also indicated that the polyimide in the composite may experience some degree of graphitization at this temperature with the assistance of graphene.²¹

XRD Studies of Heat-Treated Polyimide and Polyimide/Graphene Composite Films

XRD is an important characterization for determining the crystal structure of graphite, which is constituted by thousands of graphene sheet layers. But for exfoliated graphene and graphene dispersed well in polymer matrix, their layer-stacking regularity almost disappeared. As a result, no diffraction peak can be

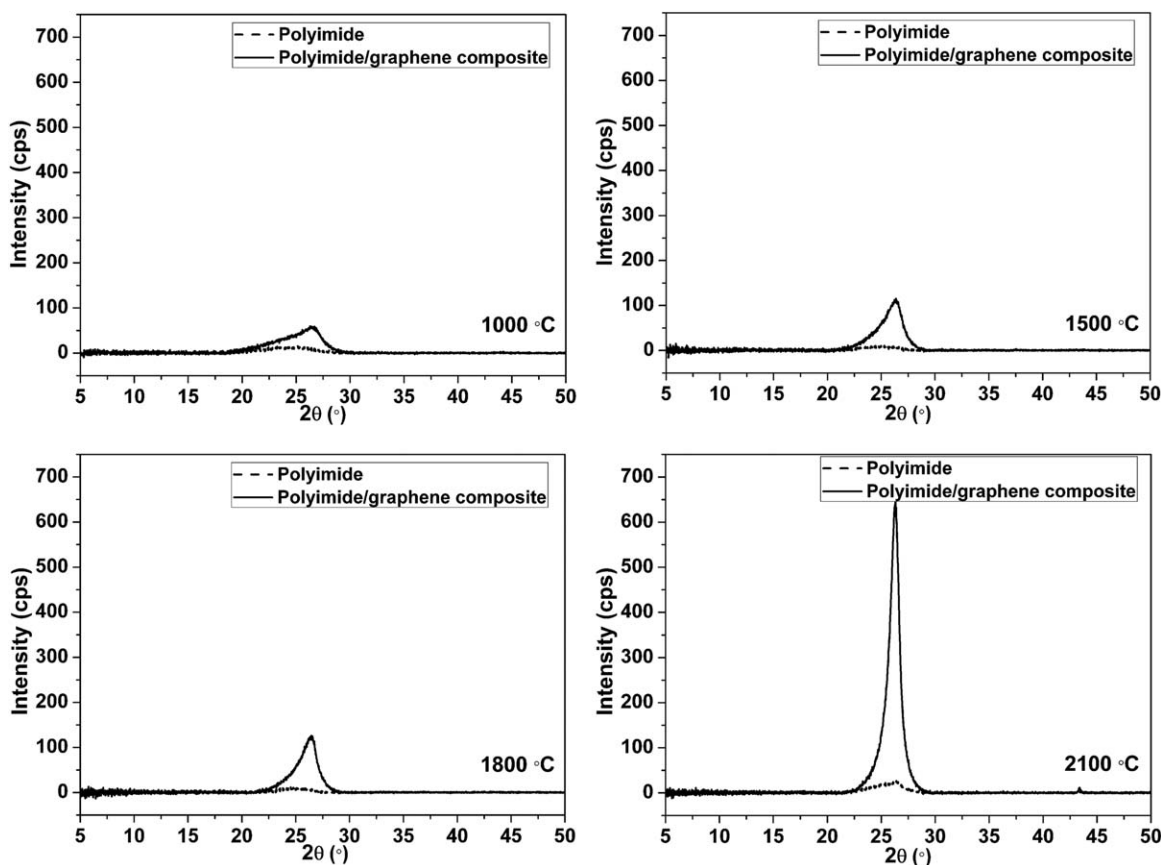


Figure 6. X-ray diffraction profile of polyimide and polyimide/graphene composite films heat-treated at different temperature for 1 h.

observed from their XRD patterns.^{39,40} In the study, thermally exfoliated graphene was dispersed well in the polyimide matrix. So, the XRD measurement could be used to characterize the graphitization process of polyimide in the polyimide/graphene composite film. Figure 6 shows the (002) diffraction peaks of polyimide/graphene composite film in comparison with that of polyimide film. The polyimide film had a broad and weak 002 profile, even though it was heat-treated to 2100°C. However, when the polyimide/graphene composite film was heat-treated to 2100°C, its (002) diffraction peak increased suddenly and was sharp.

Ideal graphite crystal is known to have an interlayer spacing of 0.3354 nm.¹⁶ According to the Bragg equation,⁴¹ the interlayer spacing of 2100°C-treated polyimide/graphene composite was 0.3386 nm. Although the interlayer spacing of 2100°C-treated polyimide/graphene composite was higher than that of ideal graphite crystal, according to the result of Konno et al., for polyimide PMDA/ODA imidized on glass, to decrease the interlayer spacing to 0.3386 nm, the heat treatment temperature should be increased to about 2500°C.⁴² So, with the assistance of graphene, the graphitization process of polyimide could be accelerated.

SEM Observations of Heat-Treated Polyimide and Polyimide/Graphene Composite Films

Graphitization, involving the joining of smaller segments of graphite layer plane together to form larger layer plane which is then translated into a proper stacking registry with neighboring

layer planes, refers to a development of the three-dimensional graphite-like structure in the initially two-dimensionally ordered carbon.^{43,44} Figure 7 shows the cross-section morphologies of polyimide film heat-treated at 2100°C and polyimide/graphene composite film heat-treated at 1000 and 2100°C. Photos (d), (e), and (f) are the enlargements of each area surrounded by a black line in photos (a), (b), and (c), respectively. For polyimide/graphene composite film, the graphene sheets were distinguishable from the polyimide matrix, and the change in the morphology of polyimide matrix with heat treatment temperature was shown clearly. After heat treatment at 2100°C for 1 h, large lamellar region could be observed clearly by the enlargement, which was indicative of formation of graphitic structure.²¹ But for 2100°C-treated polyimide film, no lamellar texture could be found and the matrix remained amorphous. The result also indicated that graphene played an important role in accelerating the graphitization process of the polyimide.

Mechanism for Acceleration in Graphitization Process of Polyimide/Graphene Composite

Many previous studies have shown that, internal stress could be developed in composites of reinforcements and carbon precursors during the carbonization process of carbon precursors, which could be used to accelerate the graphitization process of carbon precursors.^{15,16,20–22} This is because most carbon precursors show a large amount of shrinkage during carbonization, while the

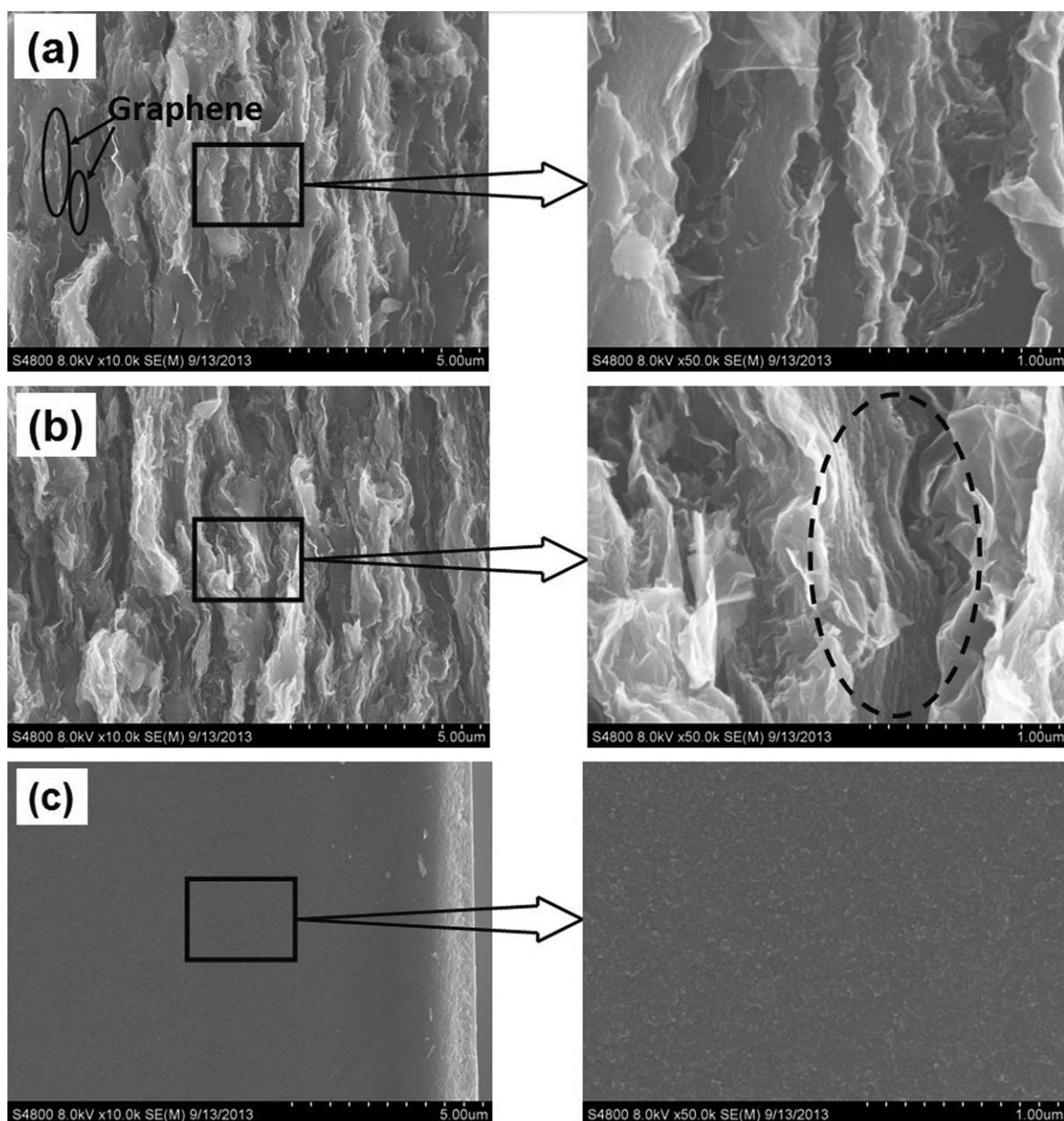


Figure 7. SEM photographs of the cross section of different films. (a) 1000°C-treated polyimide/graphene composite film; (b) 2100°C-treated polyimide/graphene composite film; (c) 2100°C-treated polyimide film.

reinforcements are dimensionally stable. The shrinkage of carbon precursors could be partially inhibited due to the presence of reinforcements. Consequently, internal stress is produced and accumulated during the carbonization process. Kimura et al. measured the stress accumulation at the boundary between carbon fiber and carbon precursor as a function of the distance from the surface of carbon fiber using a model of a thick-wall cylinder, and the maximum stress accumulated at the carbon fiber-carbon precursor interface was calculated to have possibly reached 0.4 GPa during carbonization.²⁰ As mentioned above, the shrinkage of polyimide/graphene composite film (around 14%) was much less than that of polyimide film (around 22%) after heat treatment, which was because the tough and rigid graphene could partially suppress the shrinkage of polyimide during heat treatment. This led to the development of internal stress in the

polyimide/graphene composite, which could be responsible for the acceleration in graphitization process of the polyimide in the polyimide/graphene composite film.

From reported studies about graphitization process of composites, the maximum internal stress accumulated at the reinforcement-carbon precursor interface and the internal stress decreased as the distance from the reinforcement increased.^{16,20} Therefore, the graphitization of carbon precursors was found to start at the interface between the reinforcements and carbon precursors. If the distance between the reinforcements and the carbon precursors was large enough, no acceleration in the graphitization process of carbon precursors was found to take place.¹⁶ The nonuniformity was considered to be a characteristic of the internal stress-assisted graphitization.¹⁶ Carbon fiber was

widely used as a reinforcement, and Bahl advised that the carbon fiber should be used in the chopped form to increase the stress centers.⁴⁵ In the study, thermally exfoliated graphene with high specific surface area was dispersed uniformly in the polyimide matrix. This was done to help generate more stress centers.

CONCLUSION

Different from most studies about internal stress-assisted graphitization where carbon fiber was used as the reinforcement, tough and rigid thermally exfoliated graphene with a high specific surface area was chosen as the reinforcement in the study. It was found that, after addition of graphene, the shrinkage of polyimide film in the direction parallel to the film surface during heat treatment was effectively suppressed. This phenomenon was an indication of formation of stress in the polyimide/graphene composite. As a result, a significant acceleration in the graphitization process of polyimide was found to take place. Based on the finding, we can conclude that graphene is a good choice as the reinforcement to accelerate graphitization process of carbon precursors.

AUTHOR CONTRIBUTION

Xueliang Pei: Design, preparation, characterization, data analysis, and drafting the paper; Bin Shen and Lihua Zhang: Characterization and revising the paper critically; Wentao Zhai and Wenge Zheng: Promoter of the study and revising the paper critically.

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